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# NUCLEAR ENERGY RESEARCH INITIATIVE

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## Advanced Extraction Methods for Actinide/Lanthanide Separations

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Collaborators: Argonne National Laboratory (ANL)

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The separation of An(III) ions from chemically similar Ln(III) ions is perhaps one of the most difficult problems encountered during the processing of acidic nitrate nuclear waste. In the 3+ oxidation states, the metal ions have an identical charge and roughly the same ionic radius. They differ strictly in the relative energies of their f- and d-orbitals, and in order to separate these metal ions, ligands will need to be developed that take advantage of this small but important distinction. If an efficient protocol can be developed for their partitioning, neutron bombardment can be employed to transmute actinides into products with significantly shorter radioactive lifetimes. Along with aiding the processing of acid nuclear waste streams, this methodology should ease some of the concerns expressed by the American public involving the long-term storage of nuclear waste.

With the intent to mimic the 3:1 CMPO:actinide stoichiometry of the extracted species in the TRUEX nuclear waste treatment process, a ligand system containing three pre-organized carbamoylmethylphosphine oxide (CMPO) moieties anchored onto a rigid three-fold symmetric triphenoxymethane platform has been developed for facile complexation of actinide ions and subsequent extraction from acidic nitrate nuclear waste streams. The CMPO arms on the ligands are oriented such that all three CMPO moieties can cooperatively bind a metal ion. Preliminary extraction experiments with simulated nuclear waste streams with solutions of the first generation of the ligand reveal a high affinity for the actinide thorium and a very low, constant affinity for the lanthanides across the series. Several different ligand derivatives have been prepared, and a series of distribution ratio measurements will be performed at Argonne National Laboratory with at least two lanthanides and americium to test the selectivity of the ligands for the 3+ metals. This information will be used to help design an improved ligand set.

One method to tune the actinide selectivity will be to influence the charge density of the metal and its coordination geometry. Accordingly, small alterations can be made to the ligand system to exploit these differences and further increase its affinity for actinides. Procedures have been outlined to incorporate modifications that alter the basicity of the CMPO oxygen donors as well as the distance between adjacent CMPO groups on the triphenoxymethane platform. With a wide variety of methods to alter the three arms, the binding attributes of the ligand can be subtly adjusted using the extraction data obtained from the group at Argonne to maximize the selectivity for the 3+ actinides.

The proposed work falls within the scope of fundamental chemistry program in the Nuclear Energy Research Initiative and funding from the Department of Energy will allow for a detailed examination of the An(III) binding properties of the ligands at Argonne National Laboratory. This information will be crucial for the further refinement of the C3-symmetric actinide binder at the University of Florida. The continued cooperation between the two organizations should produce an advanced extraction process for the separation of the chemically similar actinides and lanthanides found in acidic nitrate nuclear waste streams. It is envisioned that the compounds prepared during this work can be used in a process to remove the An(III) ions from nuclear waste streams immediately following the PUREX process and perhaps after concentration of the An(III) and Ln(III) ions by the DIAMEX process.